Optimization of Bleaching Earth and Extraction of Free Fatty Acid (FFA) in Palm Oil Refinery Process

SITI HAIZAN BT MOHD MUKHTAR AFFANDI

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering and Natural Resources

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2015

ABSTRACT

Physical refining has become the major processing route for crude palm oil in Malaysia. Degumming, bleaching and deodorization are essential processes that involves in palm oil refining. The purpose is the removal of gums, trace metals, pigments, peroxides, oxidation products and other breakdown products in the crude oil by adsorption on the active surface of the bleaching earth to improve colour and stability of the final oil (Siew et al., 1992). This research aims to study the Optimization of Bleaching Earth and Extraction of Free Fatty Acid (FFA) in Palm Oil Refinery Process which involves process of degumming and bleaching using neutral and acid-activated clays. Degumming is the pre-treatment stage of physical refining crude palm oil and these stages are identified as the major contributors to the total operating cost of the plant due to the cost of chemicals (phosphoric acid and bleaching earth) that are being used in these processes .Bleaching absorbs the undesirable impurities and other pigments. It also reduces the oxidation products, absorbs the phospholipids precipitated by phosphorus acid, and removes any excess present in the oil. Last stage for physical refining is deodorization. The pre-treated oil is deoerated and then heated to deodorization temperature and pressure. Under these condition , which the free fatty acids, which are still present in the oil are distilled together with the more volatile odoriferous and oxidation products such as aldehydes and ketone, which otherwise will affect the odor and the taste of the oil. In this research, a process model for degumming and bleaching operation will be designed in order to help the refiner's to predict the exact ratio of phosphoric acid and bleaching earth to the crude palm oil. By doing so, we could reduce the operating costs and time of the overall palm oil refining process.

ABSTRACT

Penapisan fizikal telah menjadi laluan pemprosesan utama bagi minyak sawit mentah di Malaysia. Degumming , peluntur dan penyahbauan adalah proses penting yang melibatkan penapisan minyak sawit. Tujuannya adalah penyingkiran gusi , logam surih, pigmen , peroksida , produk pengoksidaan dan produk kerosakan lain dalam minyak mentah oleh penjerapan di permukaan aktif peluntur bumi untuk meningkatkan warna dan kestabilan minyak akhir (Siew et al. , 1992). Kajian ini bertujuan untuk mengkaji Pengoptimuman Peluntur Bumi dan Pengeluaran Asid Lemak Bebas (FFA) dalam Proses Penapisan Minyak Sawit yang melibatkan proses degumming dan peluntur menggunakan tanah liat neutral dan asid- diaktifkan. Degumming adalah peringkat pra- rawatan penapisan fizikal minyak sawit mentah dan peringkat ini dikenal pasti sebagai penyumbang utama kepada jumlah kos operasi kilang kerana kos bahan kimia (asid fosforik dan peluntur bumi) yang digunakan dalam proses ini. Peluntur menyerap kekotoran yang tidak diingini dan pigmen lain. Ia juga mengurangkan produk pengoksidaan, menyerap phospholipid yang dihasilkan oleh asid fosforus, dan memindahkan lebihan bendasing di dalam minyak. Peringkat akhir untuk penapisan fizikal adalah penyahbauan. Minyak pra- dirawat deoerated dan kemudian dipanaskan kepada suhu dan tekanan penyahbauan. Di bawah keadaan ini, asid lemak bebas yang masih ada dalam minyak akan disuling bersama-sama dengan bendasing yang berbau busuk dan pengoksidaan produk lebih tidak menentu seperti aldehid dan keton , yang boleh memberi kesan bau dan rasa pada minyak sekali gus meningkatkan kualiti minyak yang terhasil. Dalam kajian ini, satu model proses degumming dan peluntur operasi akan direka bentuk untuk membantu penapis untuk meramalkan nisbah yang tepat asid fosforik dan peluntur bumi untuk minyak sawit mentah. Dengan berbuat demikian, kita boleh mengurangkan kos operasi dan masa proses penapisan minyak sawit secara keseluruhan.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Introduction

The background of the research which are include raw materials, process and the product that will be produce in this research. In this chapter, we will include the identification of problems, research objectives, research scopes and rational and significant of the study.

1.2 Background of Study

Palm oil is one of the various types of vegetable oils, belonging to the group called liquids, because of its fatty acids content. Oil palm tree (*Elaeis guineensis Jacq)* is one of the two most important vegetable oils in the world's oil and fats market with one hectare of oil palm producing between 10 and 35 tones of fresh fruit bunch (FFB) per year ([Hartley, C.N.S., 1988;Ma, A.N., Y. Tajima, M. Asahi and J. Hannif, 1996]).The extraction and purification processes generate different kinds of waste generally known as palm oil mill effluent (POME) (Mohd Izwan,2010) and typically,1 t of crude palm oil production requires 5–7.5 t of water; over 50% of which ends up as POME(J.C. Igwe and C.C. Onyegbado,2007) . POME has a high nutrient content (Zakaria et al. 1994), and large oil palm plantations prefer to use it directly as fertilizer. The POME is first treated to reduce the organic load (Ma et al. 1993). In crude palm oil, the amounts of such impurities vary, depending on its quality. As say by siew,1987, phosphorus varies from 10 to 40 ppm of which a portion is inorganic, and iron from 2-10 pm (Tan et al 1999).the quality of CPO is determined by its free fatty-acid content ,and the oxidative parameter(Swodoba,1982).

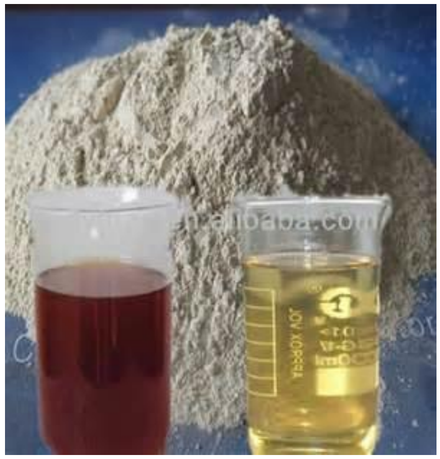

Figure 1 : Palm Oil before (left) and
after (right) Undergo Bleaching Process

Proceeded generally by degumming and refining(neutralization) processes, bleaching is required to removed specific detrimental contaminants that are not effectively removed by these processes before the oil progresses through deodorization.

Bleaching originally described as a process of mixing oil and clay adsorbent to remove color, reduces the content of chlorophyll, residual soap and gums, oxidative products, trace metals and indirectly impacts on deodorized oil color

Bleaching earth is also known as fuller's earth and is essentially a physical adsorption process using activated carbon or bleaching earth to removed undesired matters from oils. Bleaching earth is a type of clay mined in Asia, England, India and United States. Once you obtain bleaching earth you get a substance that is rich in minerals and it is used for various purposes including for bleaching, absorbing and filtering.

If bleaching earth is used for industrial purposes, the earth then has to be put through processing which involves recycling. After this recycling, the earth will be ready to be used again and it will also be in a state in which it can safely be disposed of but also beware that these substances are quite flammable and they have harmful characteristics as well. Attapulgite ,bentonite and montmorillonite clays are the most commontly found in bleaching earth.. Once obtained from the earth, this mineral-rich substance is processed and used for its absorbing, bleaching, and filtering properties.

Figure 2 : Reactor in Refining Process

1.3 Motivation and statement of problem

In the palm oil refinery, the critical part is degumming and bleaching process stage where at these stages separation of minor components must be carefully monitored (Goh *et al.*, 1985). Any imperfection during these processes will tremendously affect refining processes or the later stages and finally affect the finished product byproduct. These stages are considered as major contributors to the total operating cost of the plant due to the cost of chemicals which is phosphoric acid and bleaching earth clay that are being used in these processes.

Bleaching is one of the most cost-intensive processes for refining vegetable oils caused mainly by the consumption of bleaching agents like bleaching earth and activated carbon, oil losses in the spent bleaching and in certain cases for disposal of the spent agents. Because of these reason, all refineries to trying to find a way to reduce the cash flow out for this process as much as they can. The price of bleaching earth is RM 700-800 per MT and RM 3000 per MT for phosphoric acid and it is about 20% of total operating cost are due to bleaching process. In current situation the amounts of chemicals added in are usually fixed within typical ranges of doses usually used throughout certain period. It means that, even though the incoming CPO has lower impurities or minor components content, the amount of chemicals added would not be changed. Thus, it important to have a process model which can suggest a suitable ratio of phosphoric acid and bleaching earth for the varying CPO quality.

1.4 Objectives of research

The objectives of this research are:

1.3.1 To predict the most optimal ratio of phosphoric acid and bleaching earth for the bleaching process of crude palm oil.

1.3.2 To decrease the percentage of FFA by optimizes physical refining bleaching process condition.

1.3.3 Identification of the most optimal operating parameters and conditions for bleaching processes.

1.5 Scope of study

In order to achieve the objective, the following scopes have been identified and to be applied:

1.4.1 The effect of time contact (20, 40, 60 minutes) of bleaching clay in bleaching process

1.4.2 The effect of temperature range 60℃-90℃ in physical bleaching process

1.4.3 The effect of ratio of acid (0.05-0.1 %w) to earth clay(0.2-2.0%w) in physical refinery process and the number of experiments need to be run are determined through the design of experiment (DOE) method.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, the finding of related articles from goggle scholar, MPOB website and I-portal is needed in order to do literature review. The literature review is research done in the past by other people and it is needed to support our research objectives.

2.2 Oil Palm

2.2.1 History, habitat, tree and industrial development

The oil palm tree is a tropical palm tree and has two species which better known originally come from Guinea, Africa is originally illustrate by Nicholaas Jacquin in year of 1763 and hence, oil palm is known as *Elaeis guineensis Jacq* as after his name. Elaia is come from Greek word that means olive which indicates its fruits rich in oil. Besides that, *Elaeis guineensis* is also a member of the family *Palmae* with their subfamily, *Cocoidae* which is includes the coconut.

The most suitable area for oil palm is soil that free from draining with low pH and does not thrive at very high pH which is greater than 7.5. Its culture is well done in low altitude less than 500 m above sea level with 15˚ from the equator in the humid tropics. The soil is properly drained with distributed of rainfall of 1,800 to 2,000 mm/year but will tolerate rainfall up 5,000 mm/year. If there are three months in row, with less than 100 mm rainfall per month, productive yield will be reduced as oil palm is sensitive toward poor drainage and drought. This is one of the reason why it is agreed that oil palm *Elaeis guineensis Jacq,* is originated from equatorial tropical rain forest Africa.

Figure 3 : Fresh Fruit Bunch

The most suitable area for oil palm is soil that free from draining with low pH and does not thrive at very high pH which is greater than 7.5. Its culture is well done in low altitude less than 500 m above sea level with 15˚ from the equator in the humid tropics. The soil is properly drained with distributed of rainfall of 1,800 to 2,000 mm/year but will tolerate rainfall up 5,000 mm/year. If there are three months in row, with less than 100 mm rainfall per month, productive yield will be reduced as oil palm is sensitive toward poor drainage and drought. This is one of the reason why it is agreed that oil palm *Elaeis guineensis Jacq,* is originated from equatorial tropical rain forest Africa.

Oil palm is native to Africa, but Malaysia was the first country to embark on large-scale planting and processing. In order to boost production, Malaysia had to create and develop its own technology and adopt innovative policies. In 1917, the first commercial oil palm estate in Malaysia was set up at Tennamaran Estate, Selangor. However, in order to get through over dependence on natural rubber which are major commodity during previous years ,it was only in the 1960s, oil palms were commercially cultivated in bigger scale.(Kifli,1981) Currently, there are more than three million hectares of oil palm plantations. In total, about 90 million mt of renewable biomass (trunks, fronds, shells, palm press fiber and the empty fruit bunches) are produced each year.(M. Suhaimi and H.K. Ong,2011)

Since then, palm oil industry has expended rapidly and has emerged as the most remunerative agricultural commodity, overtaking the natural rubber (Arrifin and Fairus 2002).The present and increasing of the industry has been phenomenal and accounting for 52 percent of world production and 64 percent of world exports in 1999, Malaysia is now the largest producer and exporter of palm oil in the world, and Figure 6 below, shows world annual production and annual exports of palm oil according to the respective countries. This was complemented by the government allocating land to the poor and landless to plant more oil palm, in great part causing the area to increase from 62 000 ha in 1975 to 1.02 million hectares in 1980 and 2.03 million hectares in 1990. By 2007, there were 4.3 million hectares of oil palm, constituting nearly two-thirds of the national agricultural area. With a production of 16.20 million tonnes in 2006, Malaysia continues to be the world's largest palm oil producer. The success of the crop is largely market driven with good long term price prospects for palm oil making oil palm more attractive than most other crops. Palm oil contributes more than one-third of the national agricultural GDP, generating RM 31.81 billion in export earnings in 2006, making it one of the pillars of Malaysia's economy. At present, the industry employs more than 1.5 million people in the core and related sectors.

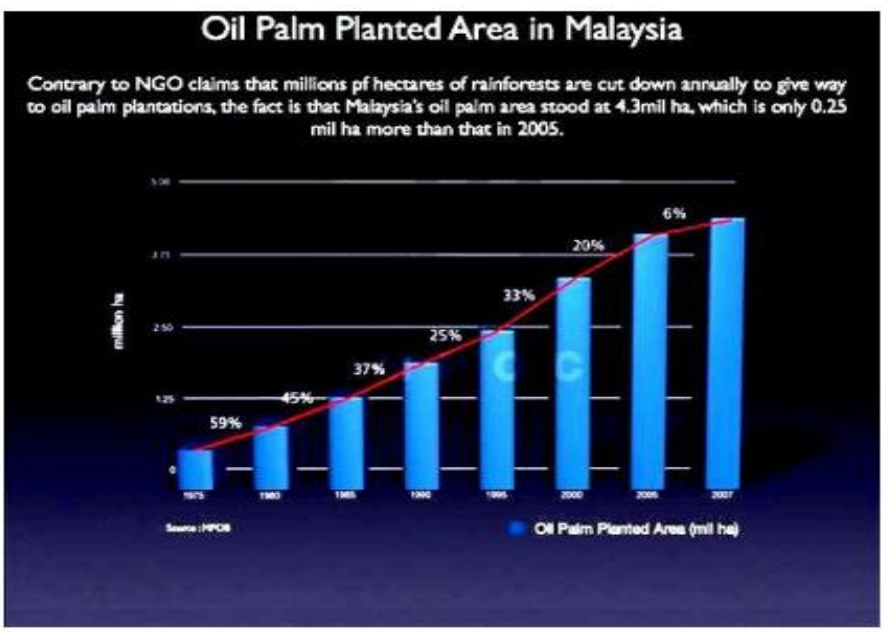

Figure 4 : Oil Palm Planted Area in Malaysia 1975-2007

Country	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
Malaysia	7,403	7,221	8,386	9,069	8,319	10,554	10,842	11,804	11,909	13,354
Indonesia	3,421	4,008	4,540	5,380	5,361	6,250	7,050	8,030	9,200	9,750
Nigeria	645	640	670	680	690	720	740	770	775	785
Colombia	323	353	410	441	424	501	524	548	528	543
Cote d'Ivoire	310	300	280	259	269	264	278	220	240	251
Thailand	297	316	375	390	475	560	525	620	600	630
Papua New Guinea	223	225	272	275	210	264	336	329	316	325
Ecuador	162	178	188	203	200	263	222	201	217	247
Costa Rica	84	90	109	119	105	122	138	138	140	144
Honduras	80	76	76	77	92	90	97	108	110	112
Brazil	54	71	80	80	89	92	108	110	118	132
Venezuela	21	34	45	54	44	60	73	80	80	79
Guatemala	16	22	36	50	47	53	65	70	81	91
Others	1,265	1,676	815	869	844	832	879	919	922	940
TOTAL	**14,304**	**15,210**	**16,282**	**17,946**	**17,169**	**20,625**	**21,877**	**23,947**	**25,236**	**27,383**

Figure 5 : World Major Producers of Palm Oil '000 tonnes (MPOB, 2003)

Country	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
Malaysia	6,750	6,513	7,212	7,490	7,465	8,911	9,081	10,618	10,886	12,248
Indonesia	2,173	1,856	1,851	2,982	2,260	3,319	4,140	4,940	6,379	6,830
Papua New Guinea	231	220	267	275	213	254	336	328	324	325
Cote d'Ivoire	148	120	99	73	102	101	72	75	65	63
Colombia	20	21	29	61	70	90	97	90	85	105
Singapore*	328	399	289	298	241	292	240	224	220	256
Hong Kong*	234	275	305	173	103	94	158	192	318	206
Others	876	791	711	860	680	787	884	1,107	956	1,083
TOTAL	**10,760**	**10,195**	**10,763**	**12,212**	**11,134**	**13,848**	**15,008**	**17,574**	**19,233**	**21,116**

Figure 6 : World Major Exporters of Palm Oil '000 tonnes (MPOB, 2003)

Natural pigments that present in vegetable oils are mainly the caused by carotenoid, giving yellow and red colors, and the chlorophylls which give green colors. Color deterioration of crude palm oil can take place during the refining process, which removes contaminants that adversely impact the appearance and performance of this oil. Many of these impurities have to be removed from the oil to achieve the high quality oil standards necessary for edible applications.

2.2.2 What is Crude Palm Oil?

There are two types of oil produced from oil palm. The first is crude palm oil (CPO) and the second is crude palm kernel oil (CPKO) from the palm kernel. The two types of oil differ in terms of chemical composition and nutritional content. Palm oil has a balanced ratio of saturated and unsaturated fatty acids while palm kernel oil has mainly saturated fatty acids (Teoh, C.H. (2002). Crude palm oil (CPO) is the oil obtained from the mesocarp part of palm oil fruit. Figure 8 shows the processes undergone by fresh fruit bunches (FFB) to produce CPO. The crude palm oil (CPO) produced, is further processed to yield either red or bleached cooking oil or detergents.

Figure 7 : Crude Palm Oil

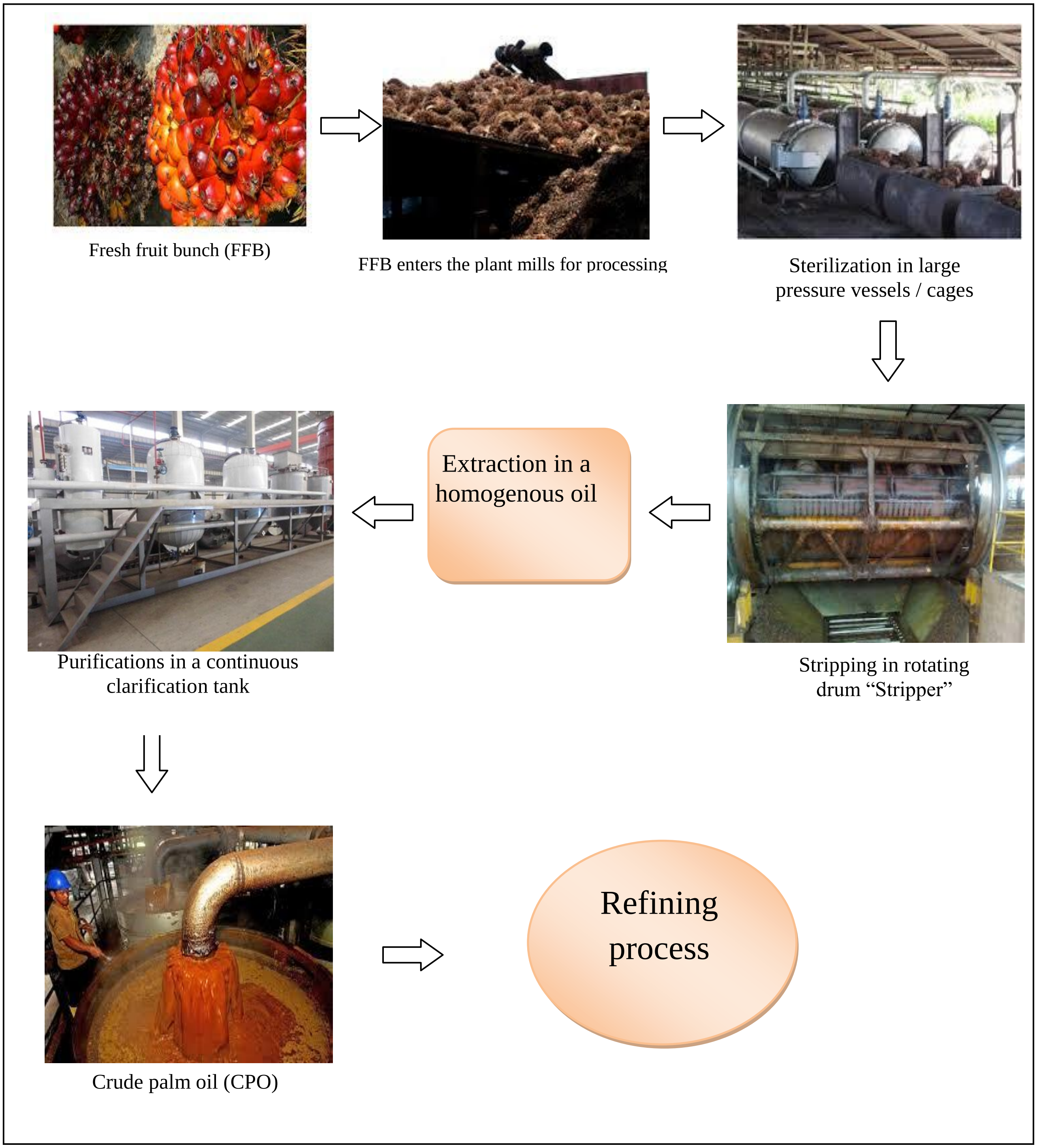

Figure 8 : Flowchart of Crude Palm Oil (CPO) Production

2.2.3 Chemistry of Palm Oil

Higuchi (1983), The empty bunch is a solid waste product of the oil palm milling process and has a high moisture content of approximately 55-65% and high silica content, from 25% of the total palm fruit stated that crude vegetables oil commonly consists of desirable triglycerides, unsaponifiable matter together with small amount of impurities (Keu, S.T., 2005). Like all oils, TGs are the major constituents of palm oil. Over 95% of palm oil consists of mixtures of TGs, that is, glycerol molecules, each esterified with three fatty acids. During oil extraction from the mesocarp, the hydrophobic TGs attract other fat- or oil-soluble cellular components. These are the minor components of palm oil such as phosphatides, sterols, pigments, tocopherols, tocotrienols and trace metals. Other components in palm oil are the metabolites in the biosynthesis of TGs and products from lipolytic activity. These include the monoglycerols (MGs), diglycerols (DGs) and free fatty acids (FFAs).

The fatty acids are any of a class of aliphatic acids, such as palmitic (16:0), stearic (18:0) and oleic (18:1) in animal and vegetable fats and oils. The major fatty acids in palm oil are myristic (14:0), palmitic, stearic, oleic and linoleic (18:2).5

The typical fatty acid composition of palm oil from Malaysia is presented in Table 2.1. Palm oil has saturated and unsaturated fatty acids in approximately equal amounts.

Most of the fatty acids are present as TGs. The different placement of fatty acids and fatty acid types on the glycerol molecule produces a number of different TGs. There are 7 to 10% of saturated TGs, predominantly tripalmitin.

The fully unsaturated TGs constitute 6 to 12%. The Sn-2 position has specificity for unsaturated fatty acids. Therefore, more than 85% of the unsaturated fatty acids are located in the Sn-2 position of the glycerol molecule. The triacylglycerols in palm oil partially define most of the physical characteristics of the palm oil such as melting point and crystallisation behaviour The crude palm oil compositions can also be classified as a mixture of 5 main chemical groups as per shown in Figure 9 below.

Group	Components in the group
Oil	- Triglyceride, Diglyceride , Monoglyceride - Phospholipids, Glycolipid and Lipoprotein - Free fatty acids
Oxidized Products	- Peroxides, Aldehydes, Ketones, Furfurals (from sugars)
Non-oil (but oil solubles)	Carotene - Tocopherols - Squalene - Sterols
Impurities	- Metal particles - Metal ions - Metal complexes
Water Solubles	- Water (moisture) - Glycerol - Chlorophyll pigments - Phenols - Sugars (soluble carbohydrates)

Figure 9 : General Composition of Crude Palm Oil (Abdul Azis, 2000)

Table 2.1: Typical Fatty Acid Composition (%) of Palm Oil

Fatty acid chain length	Mean	Range observed	Standard deviation
12 : 0	0.3	0-1	0.12
14 : 0	1.1	0.9-1.5	0.08
16 : 0	43.5	39.2-45.8	0.95
16 : 1	0.2	0-0.4	0.05
18 : 0	4.3	3.7-5.1	0.18
18 : 1	39.8	37.4-44.1	0.94
18 : 2	10.2	8.7-12.5	0.56
18 : 3	0.3	0-0.6	0.07
20 : 0	0.2	0-0.4	0.16

2.2.4 Finished Products (RBDPO) Quality

In Malaysia, the generally accepted trading specifications for crude palm oil are; 5 % maximum FFA; 2.5 % maximum moisture and impurities (Goh, 1991),while the Palm Oil Refiners Association of Malaysia (PORAM) standard specifications for refined palm oils are given in Table 2.2. Refined, bleached and deodorised palm oil is obtained from crude or semi-refined palm oil which has been bleached, deodorised and deacidified by physical means (PORIM, 2000). The melting and crystallisation characteristic of the oil can be followed using the DSC technique (Gunstone, 2011).

Table 2.2 : Standard Specification For Refined Palm Oils (Victoria et al., 2011)

Parameter	RBD Palm Oil
Free Fatty Acid,FFA (% as Palmitic)	0.1 max
Moisture and Impurities (%)	0.1 max
Iodine Value (Wijs)	50-55
Melting Point(C-AOCS Cc 3-25)	33-39
Color(5.25"Lovibond Cell)	3 or 6 red max

2.2.5 Uses of Palm Oil

As mentioned, the oil palm produces two types of oils, palm oil from the fibrous mesocarp and palm kernel oil from the palm kernel. Palm oil and palm kernel oil have a wide range of applications; about 80% are used of food applications while the rest is feedstock for a number of non-food applications (Salmiah. 2000).

Among the food uses, refined, bleached and deodorised (RBD) olein is used mainly as cooking and frying oils, while RBD stearin is used for the production of shortenings and margarine. RBD palm oil, which is the unfractionated palm oil, is used for producing margarine, shortenings, vanaspati(vegetable ghee), frying fats and ice cream (Salmiah, 2000).

2.3 Refinery Method in Industry

Refining process is an important step for the production of edible oils and fats products. The objective is to remove the impurities and other components that will affect the quality of finished product. Crude palm oil of poor quality was degummed, bleached and deodorized to evaluate the effectiveness of various bleaching clays using different dosages (Ng, Sook Kuen, 2006).

The flavor, shelf-life stability and color of the finish products need to be monitored to maintain its quality. (Leong, 1992).In industry perspective, to convert the crude oil to a quality edible oil is the main aim of refining by removing objectionable impurities in the most efficient manner to the desired levels. This also means that, where possible, losses in the desirable components are kept minimal and cost effective.

The objectionable substance or impurities in palm oil maybe biogenic synthesized by plant themselves but they can be impurities taken up by the plants from their environment (Borner et al., 1999). The impurities maybe acquired during upstream of bleaching process which are extraction, storage or transportation of the crude palm oil from mill to the refinery. It is important to have proper refining process in order to produce high quality of finished products with specified quality range and meet users' requirements.

Parameter that used to assess the efficiency of various stages of a refining process is called Refining factor (RF). It is dependent upon the yield of the product and the quality of the input and it is calculated as:

$$RF = \frac{oil\ loss\%}{FFA\%}$$

The RF is usually quantified for various stages of refining process individually and monitoring of the RF in the refinery is usually by means of weight calculated from volumetric measurements adjusted for temperature or by using accurate cross-checked flow meters.

There are 2 basic types of refining technology available for palm oil:

(i) Chemical (alkaline) refining

(ii) Physical refining

The differences between these 2 types are basically based on the type of chemicals used and mode of removing the FFA.

Table 2.3: Basic Step of Refining Process (Ng, Sook Kuen, 2006).

Alkali or chemical refining	Main groups of compound removed	Physical refining
Degumming	Phospholipids	Degumming
Neutralization	Free fatty acids	
Bleaching	Pigments / metals / soaps	Bleaching
Winterization	Waxes / saturated triacylglycerols	Winterization
Deodorization	Volatiles / free fatty acids	Deodorization / deacidification

2.3.1 Physical Refinery

Physical refining of vegetables oils is a distillation process. It appears to practically replace the use of chemical (alkali) refining in palm oil as the consequence of high acidity content (FFA) in chemically refined oil. The deacidification (deodorisation) process stage in the physical refining is able to overcome such situation.

Apart from that, according to the literature, this method is preferred because it is acknowledged to be suitable for low-content phosphatides vegetable oil such as palm oil. Thus, physical refining is proven to have a higher efficiency, less losses (refining factor (RF) < 1.3), less operating cost, less capital input and less influent to handle .

2.3.1.1 Dry Degumming

Degumming process is mainly to remove phospholipids or gums from the crude oil. There are two types of phospholipids present in crude oils according to their level of hydration which is hydratable and non-hydratable ones, the latter mainly present as calcium and/or magnesium salts of phosphatidic acid and phosphatidylethanolamine. Most of the phospholipids are hydrated and are insoluble in the oil if treat with water. Further filtration or centrifugations are needed to separate the hydrated compounds efficiently. The oil is usually treated with phosphoric acid for the elimination of the non-hydratable fraction, (0.05 to 1%), which chelates the Ca and Mg converting the phosphatides into the hydratable forms. Analysis of phosphorous prior to acid treatment is necessary to ensure that the acid dosage is correct due to the variable content of phospholipids in crude oils, especially when the content of Ca and Mg salts is high.

The degumming step can be eliminated depending on the oil composition and during the next step of neutralization; the phosphatides are also removed along with the soaps. Furthermore, degumming is mandatory for physical refining and the content of phosphorous after degumming should be lower than 10 mg/kg.

2.3.1.2 Bleaching Process

Bleaching is a treatment that removes the colour substances and other impurities such as fat in oil. The usual method of this process is by adsorption of the impurities on an adsorbent material or bleaching agent.

This step is applied to both physical and alkali refining, where the hot oil is slurried with acid-activated bleaching earth .Then, adsorption of colour bodies, trace metals and oxidation products such as residual soaps and phospholipids remaining will takes place.

The reaction time has to exceed 15 minutes and cannot more than 30 minutes at optimal bleaching temperatures for the great adsorption of oxidation products to be produce. The removal of chlorophyllic pigments is very important since they are not eliminated in any other stage of refining, as carotenoid compounds are in deodorization. Moreover, because of their iron content in the activated earths filtration must eliminate completely the activated earths as the presence of traces act as prooxidants during oil storage.

Although synthetic silicas and active carbons are applied in industrially, acid-activated clays are the major adsorbent used nowadays. Active carbons are used to eliminate polycyclic aromatic hydrocarbons (PAH) from some oils, especially fish oils and pomace oils, while synthetic silicas are good in adsorbing secondary oxidation products, phospholipids and soaps (Leon et all,2003).

Two types of adsorption occur between the compounds to be adsorbed and the absorbent and this is the critical part in order to obtain good quality oils. Because of the need to control the presence of refined oils in virgin oils, chemical changes taking place at this stage have been well studied in olive oil. The two main reactions found in all the vegetable oils are the following:

Figure 10 : Sunflower

- Hydroperoxides decomposition. Previous steps do not modify the peroxide value and it may even increase if air is available in the earlier stages. But, during bleaching, hydroperoxides decompose to form volatiles and oxidized triacylglycerols containing keto and hydroxy functions. After bleaching, there should be no peroxide value, but the significant increase in the anisidine value is detected where there are presence of aldehydes and ketones .
- Alcohols dehydration. Partial dehydration of hydroxyl is perform by earth catalysis.A rapid increase in UV absorption at 232 nm is observed as the function is at an allylic position because of the formation of conjugated dienes from oleic acid hydroperoxides and in UV absorption at 268 nm due to formation of conjugated trienes from linoleic acid hydroperoxides. Besides, sterols undergo significant dehydration and the formation of the